Sensing properties of perovskite oxide $La_{1-x}Sr_xCoO_{3-d}$ obtained by using pulsed laser deposition

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Summary: *$La_{1-x}Sr_xCoO_{3-d}$ belongs to the group of perovskite oxides of the ABO_3 structure, with a trivalent rare earth in the A position (La) and a trivalent metal ion in the B position (Co). Doping with divalent Sr-ions at the trivalent La-positions creates oxygen vacancies which give the oxide catalytic properties to H_2O_2. However, the conventional techniques which are used to prepare this oxide such as chemical methods, are not suitable for making a thin film. In this paper, a thin layer of $La_{1-x}Sr_xCoO_{3-d}$ (x= 0.5) perovskite oxide is deposited on a Pt electrode by using the Pulsed Laser Deposition technique. The catalytic properties of this perovskite oxide to hydrogen peroxide due to the presence of the oxygen vacancies will be discussed. The results show the possibility to use this perovskite oxide as a sensing material for potentiometric hydrogen peroxide sensors.*

Keywords: *perovskite oxide, $La_{1-x}Sr_xCoO_{3-d}$, pulsed laser deposition, hydrogen peroxide*
Category: *2 (Materials and technology) or 5 (Chemical sensors).*

1 Introduction

$La_{1-x}Sr_xCoO_{3-\delta}$ belongs to a group of perovskite oxides of the ABO_3 structure with a trivalent rare earth in the A position (La) and a trivalent metal ion in the B position (Co). The structure of the $LaCoO_3$ perovskite oxide consists of CoO_6 octahedra and the La^{3+} ions, which are inserted between the CoO_6 octahedra. When the trivalent La^{3+} ions in $LaCoO_3$ are replaced by divalent earth alkaline ions Sr^{2+} to form $La_{1-x}Sr_xCoO_{3-\delta}$, a positive charge is generated. Because the Co^{z+} ions can have a different oxidation state, the charge neutrality is maintained by the formation of oxygen vacancies and a change in the valence state of the Co^{z+} ions. Therefore, the oxide has an oxygen deficiency, δ, due to the high oxygen vacancy concentration.

This type of perovskite oxides is a promising candidate for solid oxide fuel cells, oxygen separation membranes and sensor material [1]. Different types of the perovskite oxides, which are synthesized by chemical methods, have been used as a material for hydrogen peroxide sensing. However, the response time of the sensor is quite low due to the long time it takes for the hydrogen peroxide to diffuse into the thick layer of the perovskite oxide. Among the existing deposition methods, the Pulsed Laser Deposition (PLD) is a suitable technique for the fabrication of a perovskite oxide thin film. This technique allows the stoichiometric transference of the deposited material from target to substrate [2]. In this paper, we show the possibility to obtain a thin $La_{1-x}Sr_xCoO_{3-\delta}$ (x=0.5) perovskite oxide film by using the PLD technique and its sensing properties to hydrogen peroxide.

2 Experiments

The $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film is deposited on platinum electrodes which were sputtered on a $Ta_2O_5/SiO_2/Si$ wafer, using the setup as shown in Fig. 1. During the deposition process, a metallic shadow mask was placed on top of the substrate to shield the platinum electrical contacts from undesired deposition of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$. The ablation process of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ is realized by a spatial uniform 248 nm excimer laser beam. The deposition time was varied from 5 to 7 min depending on the required thickness of the film. The thickness of the film was estimated to be about 75 nm after 5 min of deposition. After deposition, the sample was cooled down to room temperature in an O_2 flow. The annealing in the oxygen environment is necessary to obtain a stable composition and to create the oxygen vacancies in the perovskite oxide film. Finally, the wafer was diced in separated devices and encapsulated with Hysol®.

The sensing properties of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film to hydrogen peroxide is characterized in a phosphate buffer (pH = 7.1) containing 0.1M KCl. All chemicals used (Merk, Fluka) were of analytical reagent grade.

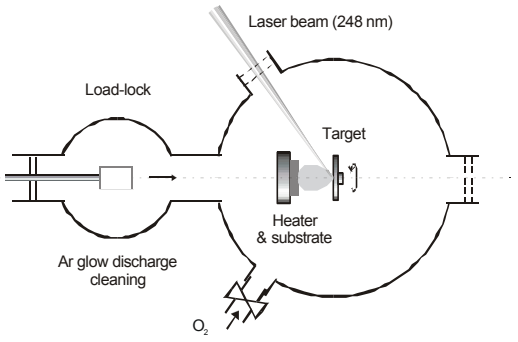

Fig. 1: Pulsed Laser Deposition system.

3 Results and discussions

The $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin film shows catalytic properties to hydrogen peroxide. The potential response of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ electrode to a change in the hydrogen peroxide concentration has been measured with respect to a saturated calomel electrode (SCE) and is shown in Fig. 2.

The response time of the electrode potential to hydrogen peroxide is estimated to be about 15 min, which is quite long due to a low exchange-current density between hydrogen peroxide and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$. The electrode potential response depends on the logarithm of the hydrogen peroxide concentration with a slope of 130 mV/dec (see Fig. 3).

The high sensitivity of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ to hydrogen peroxide is suggested to be caused by a change in the oxygen vacancy concentration in $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ during its reaction with hydrogen peroxide:

$$H_2O_2 + 2e^- + V_O^{\cdot\cdot} \xleftrightarrow{K_0} H_2O + O_L^x \qquad (1)$$

where $V_O^{\cdot\cdot}$ and O_L^x are the oxygen vacancy and the bound lattice oxygen, respectively. The reaction constant, K_0, of reaction 1 depends on the catalytic properties of the perovskite oxide, which is influenced by the strontium doping level in the perovskite oxide.

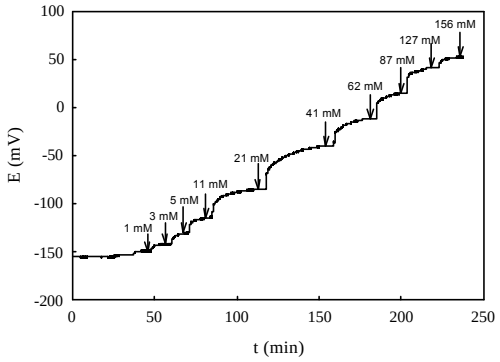

Fig. 2: Potential of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ electrode depends on the hydrogen peroxide concentration.

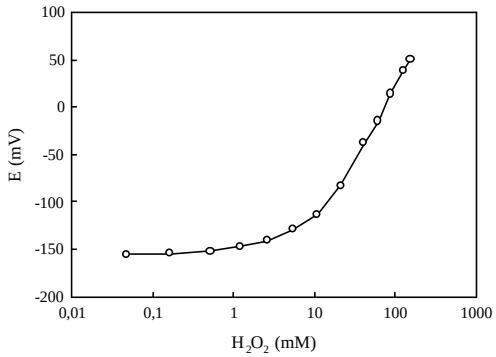

Fig. 3: Potential of the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ electrode as a function of the hydrogen peroxide concentration.

The investigation of the oxygen vacancy concentration in $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ during its reaction with hydrogen peroxide is done by means of the corresponding work function measurement. For this purpose, a thin layer of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ has been used as a gate material for an ^{E}MOSFET. The working principle of the FET and the setup for the work function measurements have previously been reported in [3].

Using the ^{E}MOSFET based structure, the change in the work function of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ due to the presence of hydrogen peroxide can be measured as a change in the threshold voltage, V_T, of the FET. In addition, due to low exchange current density between hydrogen peroxide and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, a small external DC current is used to accelerate the hydrogen peroxide decomposition and therefore to force the reaction between hydrogen peroxide and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$. As seen in Fig. 4, at an applied positive current of 50 nA, the threshold voltage of the FET increases with increasing the H_2O_2 concentration.

Acknowledgements

The authors would like to thank Johan Bomer and Frank Roesthuis for technical support. The Dutch Technology Foundation (STW) is acknowledged for financial support.

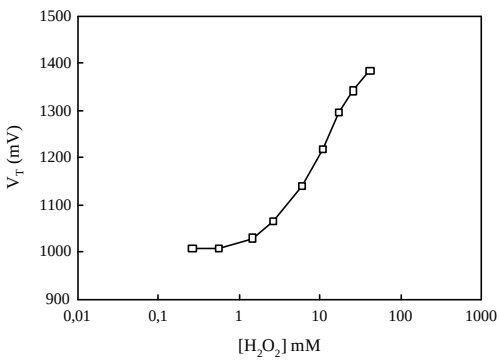

Fig. 4: Threshold voltage of the FET having a $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ gate as a function of the H_2O_2 concentration at the applied positive current of 50 nA.

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